Groundwater Monitoring for Nitrates in the Agnew-Carlsborg Area, Clallam County, Washington

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Summary

In the Spring of 2004, Clallam County Environmental Health Services (EHS) prepared to monitor groundwater quality in the Agnew and Carlsborg areas of eastern Clallam County, Washington. A Quality Assurance Project Plan (QAPP) was approved by WA Dept. of Ecology (Ecology) in May 2004, and sampling was conducted accordingly in late May and June. Twiss Analytical Laboratories in Poulsbo, WA, analyzed samples for nitrates and these results are presented in tabular form in Appendix A, and mapped in Figures 3 through 6.

While the majority of samples indicate "good" groundwater quality, three of the 125 wells tested have nitrate levels in exceedence of the drinking water standard of 10 mg/L nitrate (as N). In these instances a history of nitrates near or above this level has been documented, particularly in a portion of the Agnew community near Barr Road. More than a third of all wells tested have nitrates at or above 1 mg/L, the level considered to indicate human-caused degradation. The maximum level measured was 18.9 mg/L and the median was 0.32 mg/L. Table 1 shows historical and current nitrate levels for wells with confirmed historical data.

The presence of "hot spots" where unusually high nitrates are found highlights the importance of protecting the wider region's relatively uncontaminated groundwater quality. Sources of nitrate contamination likely include sewage, animal waste, and inorganic fertilizers. Nonpoint pollution is by nature difficult to identify and remediate. Recommended actions which will assist in resolving contamination problems include monitoring for traceable compounds, identifying and repairing inadequate well seals, continuing inspections of farms and on-site septic systems, educating residents on groundwater quality protection measures, and researching groundwater flow patterns in the areas with highest nitrate concentrations.

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Background and Problem Statement

Over the past three decades, Clallam County has experienced much of its growth in the unincorporated, rural areas of the county. This increased growth is creating pressures on water quality, particularly in the Dungeness Watershed where the relatively dry climate of the Olympic rainshadow attracts newcomers to the area. The primary change has been conversion of agricultural and forested lands to residential development.

For example, the number and density of on-site sewage systems have increased in non-sewered portions of the Sequim-Dungeness area corresponding with the population increase in recent years. Thomas et al. (1999) estimated that 7,000 on-site systems existed here in 1996, and County records indicate that about 300-400 new systems are permitted each year for that area. Septic systems are a known source of nitrate in groundwater, though the actual loading differs from system to system depending on the type of system, the soils, and the users. Other sources of nitrate include the storage and application of dairy wastewater and manure, and inorganic fertilizer application in domestic and commercial settings.

The relatively shallow depth to groundwater and lack of a low permeability layer in some areas makes the widespread surficial aquifer vulnerable to contamination from land uses above. Figure 1 shows the study area and critical aquifer recharge areas (areas susceptible to groundwater contamination). A statistically significant increase in nitrate since 1980, though slight, was reported for the greater Dungeness watershed by Thomas et al. (1999). The median nitrate concentration in groundwater in residential areas (1.3 mg/L) was higher than in agricultural (0.55 mg/L) or natural grassland or forest areas (0.12 mg/L). Further, nitrate values were highest in residential areas with a high density of on-site systems and lowest in low density areas. The Washington State Department of Health has established a 10 mg/L drinking water standard (Maximum Contaminant Level or MCL) for nitrate-N in public water supply systems (Chapter 246-290 WAC). The criterion for nitrate-N in the Washington State Water Quality Standards for Ground Waters (Chapter 173-200 WAC) is also 10 mg/L.

This groundwater quality study is part of a larger grant project addressing current surface and ground water quality problems in the Dungeness watershed. The objective of the groundwater monitoring is to determine the extent of nitrate contamination in the Agnew and Carlsborg areas of the watershed (see Figure 1) due to documented nitrate concentrations in these areas exceeding the drinking water standard (CCEHS 2002). As mentioned above, nitrate is an indicator of groundwater contamination from various sources, including on-site sewage, commercial or residential fertilizers, and manure. Probable sources of contamination were identified, however, given the complexity of the local hydrogeology and the variety of nitrate sources, the project budget did not allow for specific source identification.

The regional hydrogeology of the greater Dungeness watershed includes alternating aquifers and confining layers with a northward slope (see Figure 2) and generally northward-flowing groundwater. In Agnew, Ecology measured water levels and may have found evidence of a north-northwesterly flow direction between Spring and Barr Roads, and a cross-gradient in the Barr and Abbott Road area where the majority of contamination had been identified (Kimsey 2004).

Sinclair (2003) found that nitrate concentrations in eight wells in Agnew and Carlsborg tended to be highest in June and lowest in December. Because sample collection for this project occurred in May and June, nitrate concentrations are expected to be near the annual high. The study area for this project is very similar to that for Sinclair 2003, but this project utilized a broader sample of wells both geographically and depth-wise (Sinclair focused on the shallow aquifer). Some wells included in previous projects were utilized for this project in order to document changes in nitrate concentrations over time.

Methods

This study involved collection of a limited number (19) of groundwater samples from the study area by EHS staff (Ann Soule) in late May and June, 2004. All these samples were analyzed for nitrates and total coliform bacteria at accredited laboratories. Soule purged well water, measured field parameters, and collected samples according to a Quality Assurance Project Plan (Soule 2004) approved by Ecology. Field measurements included static water level (when possible), temperature, pH, dissolved oxygen, and conductivity.

To maximize the geographic distribution of nitrate data obtained during this study, public participants submitted samples that supplemented EHS samples. It has been found (Soule 1992; Erickson 2000) that nitrate samples collected by the public when participants follow explicit sampling instructions can yield results as reliable as samples collected by staff trained in standard scientific protocols. Most participants heard of the free nitrate testing through the media or local newsletters, however, owners of wells with historical data (e.g., from projects by USGS, Ecology, or the County) were solicited by direct mailings. EHS requested public participants to follow explicit instructions, complete a questionnaire about the procedure they used (and well, water quality, and land use information), and submit their samples to pre-determined sites for storage and transfer to the laboratory. Soule collected duplicate nitrate samples from a "QC group" consisting of 10% of publicly-sampled wells, so that results could be compared to verify public sampling technique. Field measurements and bacteria samples were taken for this QC group.

All nitrate samples were kept cool and preserved, when necessary, with sulfuric acid (in accordance with the QAPP) prior to transfer to Twiss Analytical Laboratories for analysis of nitrate-nitrite as N (otherwise referred to in this report as "nitrates"). Bacteria samples were submitted to Clallam County Environmental Health Drinking Water Laboratory for analyses of total coliform and E. coli.

Results

Nitrate results for 125 wells are presented in Appendix A, along with information obtained from the questionnaire submitted by each participant. The questionnaire data confirms the well depth for 85% of all participants, and also includes well history and landscape management practices.

<u>Extent of nitrate contamination</u>

Figures 3 through 6 illustrate the geographic distribution of nitrate concentrations. (Note that data markers on these maps are located based on the street address for the property, and displayed at the site of the driveway rather than actual well location.) The number shown above each marker indicates well depth; a "0" indicates well depth is unknown.

In Agnew, Thomas et. al. (1999) report that the shallow, partially confined aquifer extends to a maximum depth of 200 ft. below ground surface. There is a cluster of wells with nitrate levels elevated above 1 mg/L between Abbott and Barr Roads and Old Olympic Highway (see Figure 4). Within this "cluster," two wells contain nitrates in exceedence of the drinking water standard (10 mg/L); all others have levels ranging from undetected to 5 mg/L.

The confined, middle aquifer in this area is 180 ft. at its shallowest (western area), and 350 ft. below ground surface at its deepest. Only two study wells are completed in this aquifer in the Agnew area, and both have less than 1 mg/L nitrates. There are no data for this area from the lower aquifer.

In Carlsborg, Thomas et. al. (1999) report that the shallow, partially confined aquifer extends to approximately 150 ft. below ground surface. All but two wells in the study from this area tap the shallow aquifer. There is no discernable pattern to the nitrate levels in this aquifer elevated above 1 mg/L, however, there is a noticeable gap in geographic coverage for the central area, surrounding the old mill workers' neighborhood and the industrial park (see Figure 5).

In this area the confined, middle aquifer is at a depth of about 200 ft. and the lower aquifer is around 300 ft. below ground surface. Of two study wells from the Carlsborg area, one is at 202 ft. and has a nitrate level less than 1 mg/L. The other, at 300 ft., has 3.58 mg/L nitrates.

A third cluster of wells with elevated nitrates is the area between the lowest two miles of McDonald Creek and Kitchen-Dick Road (see Figure 6).

Possible nitrate trends

Table 1 shows data for study wells for which we also have historical data from previous research by USGS, Ecology, or as part of a Clallam County grant. Note that these data are sorted by well depth below ground surface; all are likely in the shallow aquifer except the last two entries. While these data were not analyzed for the statistical significance of the changes that are apparent, they illustrate that nitrate concentrations within aquifers change over time. As sources of contamination, recharge, and groundwater flow patterns change, so-called "hot spots" move around as well.

Public sampling for nitrates and data quality assessment

Results of a paired-comparison statistical test indicate no significant difference between the results of nitrate samples collected by the public vs. staff within 10 days of one another. Appendix B contains specific results for this test, as well as for other assessments of nitrate data quality including field and laboratory precision, analytical bias, and completeness. Results of these assessments indicate that all measurement quality objectives listed in the project QAPP were met.

Bacteria

Of 13 wells tested for total coliform and E. coli bacteria, four (31%) had positive total coliform results (E. coli was not detected in any samples). Two of these wells are located in Carlsborg, with depths of 79 and 202 feet; the third is in Agnew with a depth of 91 feet; the fourth is east of the mouth of McDonald Creek, and is 79 feet deep. In each of these cases, owners disinfected their water system.

Field parameters

For wells visited by EHS staff, several field parameters were measured with the following results:

Parameter	Number of meas.	Min	Median	Max
Temperature (^oC)	15	8.8	11.2	12.3
pH (standard units)	15	7.04	7.37	8.09
Conductivity (microsiemens/cm at 25^oC)	15	111	263	460
Dissolved Oxygen (mg/L)	12	1.2	2.6	8.2
Purge rate (gal/min)	14	4	8	12

Conclusions

On June 30, in Agnew, EHS sponsored a neighborhood meeting for Agnew and Carlsborg to present the regional results of the project and discuss potential next steps as well as groundwater protection in general. Representatives from Ecology and Clallam Conservation District were present and contributed to the discussion of potential sources and strategies for dealing with the problem.

The general pattern and concentrations of nitrate distribution found in this study are consistent with Thomas et. al. 1999 and Soule 1993, where "hot spots" of relatively high nitrate concentrations are found, surrounded by fairly low concentrations region-wide. In the Agnew area, much higher levels are now found than previously reported. Unpublished results from EHS monitoring in that area from 1999-2002 (CCEHS 2002) suggest similar patterns and concentrations to data from this study.

Potential sources of nitrate contamination include sewage, animal waste, and inorganic fertilizers. In addition, contamination from historical farming and irrigating activities could migrate slowly through the unsaturated zone and may cause degradation as it enters the aquifer (Thomas et. al. 1999). Kimsey (2004) reports the following:

- Nitrogen contamination of groundwater can occur if on-site sewage systems are improperly installed, or improperly operated and maintained. In addition, groundwater cannot assimilate the nitrogen load from septic systems if the density of systems is too high.
- An Agnew dairy adjacent to several wells with elevated nitrates was found to be in compliance by an inspector from Ecology on 5/10/00 as well as 12/12/02, when it received an extension until 12/04 to fully implement their dairy nutrient management plan.
- Residents must be diligent about following the label requirements for fertilizer use to assure that groundwater under their property will not become contaminated by their activities. This also includes animal management. It is important to make sure that the wellhead is protected from animals which also contribute a nitrogen load.

Factors influencing nitrate concentrations found in study wells include:

- Integrity of the surface seal intended to seal the well casing from contamination at or near the land surface, and
- Location of the well screen and/or perforations in the casing (i.e., if the well is 200 ft. deep but the casing is perforated at 50 ft., then well water from the deep, protected aquifer mixes with shallow, unprotected aquifer water).

In 2001, an Ecology well inspector found that 50% of the wells under study in Agnew at the time had insufficient surface seals (and that 100% had some type of construction or maintenance problem). A poorly constructed well, such as one without a surface seal, can provide surface contaminants a direct conduit to ground water. (Kimsey 2004)

There is no consistent pattern in the location or depth of wells with total coliform bacteria, nor was one expected since this type of bacteria is not known to persist in aquifers. Bacteria found in drinking water tend to be localized to the infrastructure itself and can usually be remedied using standard disinfection procedures. However, the high percentage of positive total coliform samples (31%) is surprising and suggests that individual, un-regulated well owners should check for bacteria on a frequent and regular basis. (Regulated systems test for bacteria monthly or yearly, depending on the population served.) The state standard for total coliform bacteria in drinking water is zero.

Recommended follow up work includes:

- Monitoring for specific parameters that may be traceable to specific sources;
- Investigation of well construction and seals for wells with extreme nitrate concentrations;
- Intensified research of groundwater flow patterns around the areas of highest concentration;
- Separate analyses of nitrate data for each sub-area and aquifer; and
- Mitigative measures such as
    - Continue to assess dairy's performance;
    - Continue to inspect on-site septic systems;
    - Repair inadequate wells to meet construction standards (e.g., well seal replacement);
    - Provide education on fertilizer use, especially by residential users; and
    - Provide education of animal management for small farms and all residents.

Bibliography

Bennett, Aimee. April 12, 2004. Personal communication.

Clallam County Environmental Health Services. 2002. Unpublished data collected by staff from 1999-2002.

Erickson, Denis. 2000. Northcentral Sumas-Blaine Surficial Aquifer Nitrate Characterization Project - June 1999. Washington State Department of Ecology Environmental Assessment Program, Olympia, Washington. 13 pgs. + appendix.

Erickson, Denis. 2002. Monitoring for Nitrate Trends in the Central Sumas-Blaine Surficial Aquifer: Quality Assurance Project Plan. Washington State Department of Ecology Environmental Assessment Program, Olympia, Washington. 18 pgs.

Erickson, Denis. March 29, 2004. Personal communication.

Jelverson, Dennis. April 12, 2004. Personal communication.

Johnson, Art, and Barb Carey. 2003. Screening for Pharmaceuticals in Wastewater Treatment Plant Effluents, Groundwater, and Surface Water in the Sequim-Dungeness Area: Quality Assurance Project Plan. Washington State Department of Ecology Environmental Assessment Program, Olympia, Washington.

Jones, M.A. 1996. Delineation of Hydrogeologic Units in the Lower Dungeness River Basin, Clallam County, Washington. U.S. Geological Survey Water-Resources Investigations Report 95-4008. 11 p. + 1 plate.

Kimsey, M. 2004. "Groundwater Investigation of the Nitrate and Bacterial Contamination in Agnew, WA." Washington State Dept. of Ecology Environmental Assessment Program, Olympia, Washington. 4 pgs.

Kirchmer, Cliff (Washington Dept. of Ecology QA Officer). April and May, 2004. Personal communication.

Lombard, Stuart and Cliff Kirchmer. 2001. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Olympia, Washington. 37 pgs.

Simonds, F. W. and K. A. Sinclair. 2002. *Surface Water-Ground Water Interactions Along the Lower Dungeness River and Vertical Hydraulic Conductivity of Streambed Sediments, Clallam County, Washington, September 1999-July 2001.* USGS Water-Resources Investigations Report 02-4161; Washington State Department of Ecology Report 02-03-027. 62 pgs.

Sinclair, Kirk. 2003. Groundwater Quality in the Agnew and Carlsborg Area, Clallam County, December 2000-September 2002. Washington State Department of Ecology Environmental Assessment Program, Olympia, Washington. 30 pgs.

Sinclair, Kirk. April 2004. Personal communication.

Soule, Ann. 1992. Sequim-Dungeness Groundwater Monitoring: Quality Assurance Project Plan. Clallam County Dept. of Community Development, Water Quality Office, Port Angeles, Washington. 28 pgs.

Soule, Ann. 1993. Mass Sampling for Nitrates in Groundwater. Poster presentation for various conferences on the results of the home water testing event conducted in eastern Clallam County in August 1992.

Soule, Ann. 2004. Groundwater Monitoring for Nitrates in the Agnew-Carlsborg Area: Quality Assurance Project Plan. Clallam County Environmental Health Services, Port Angeles, Washington. 16 pgs. plus figures and appendices.

Stallman, R.W. 1971 (reprinted in 1976 and 1983). Techniques of Water-Resources Investigations of the USGS, Chapter B1: Aquifer-Test Design, Observation and Data Analysis. 26 pgs.

Thomas, B.E., L.A. Goodman, and T.D. Olsen. 1999. Hydrogeologic assessment of the Sequim-Dungeness Area, Clallam County, Washington. U.S. Geological Survey, Water-Resources Investigations Report 99-4048, 165 p.

Twiss, Steve. March – June, 2004. Personal communication.

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This report includes the following items inserted after this point:

Table 1. Historical and current nitrate concentrations (sorted by well depth)

			Nitrates (NO3 + NO2 as N) mg/L										
			USGS				**MSE**		**SWI**	**Carlsb.**	**Intensive**	**USGS**	**A-C**
WELL ID	*DEPTH*	*ELEV.*	**'6/80**	**'8/90**	**'9/90**	**'3/91**	**'8/92**	**'9/92**	**'6/93**	**'9/93**	**'6/94**	**8/96**	**'6/04**
30N/04W-04P91	*?*	120		10.1	11.4	10.9		20			4.1		**4.13**
30N/04W-22D72	*?*						<0.01	0.05		<0.01			**0.05**
30N/04W-11R06	22	130	0.05							0.042			**0.02**
30N/04W-22D71	25						10	11		12			**14.9**
31N/04W-27R01	53	35	0.03						1.4				**2.13**
30N/04W-21G03	54	261	2.5	2.94	4.44	3.25	2.5						**0.62**
30N/04W-15G03	55	150	1.3	2.53	2.39	2.16				1.8			**4.53**
31N/04W-26M02	59	45							1.2				**1.40**
30N/04W-04P92	60	120					11	9.5			6.7		**7.11**
30N/04W-04N04	70	120					<0.01				0.017		**0.06**
30N/04W-11J01	76	122	0.14							0.79		0.12	**0.09**
30N/04W-22H72	79									2.9			**9.48**
30N/04W-17B01	91	179	0.45	0.966	0.829	0.55	0.87					1.3	**0.70**
31N/04W-25N05	103	80	0.07						0.31				**0.27**
30N/04W-05J02	111	110	2.2	11.2	9.78	9.86		8.9	8.5		4.8		**2.65**
30N/04W-23E03	202	240	0.19							0.36			**0.32**
30N/04W-07N01	281	167	0.02				<0.01		<0.01				**<0.01**

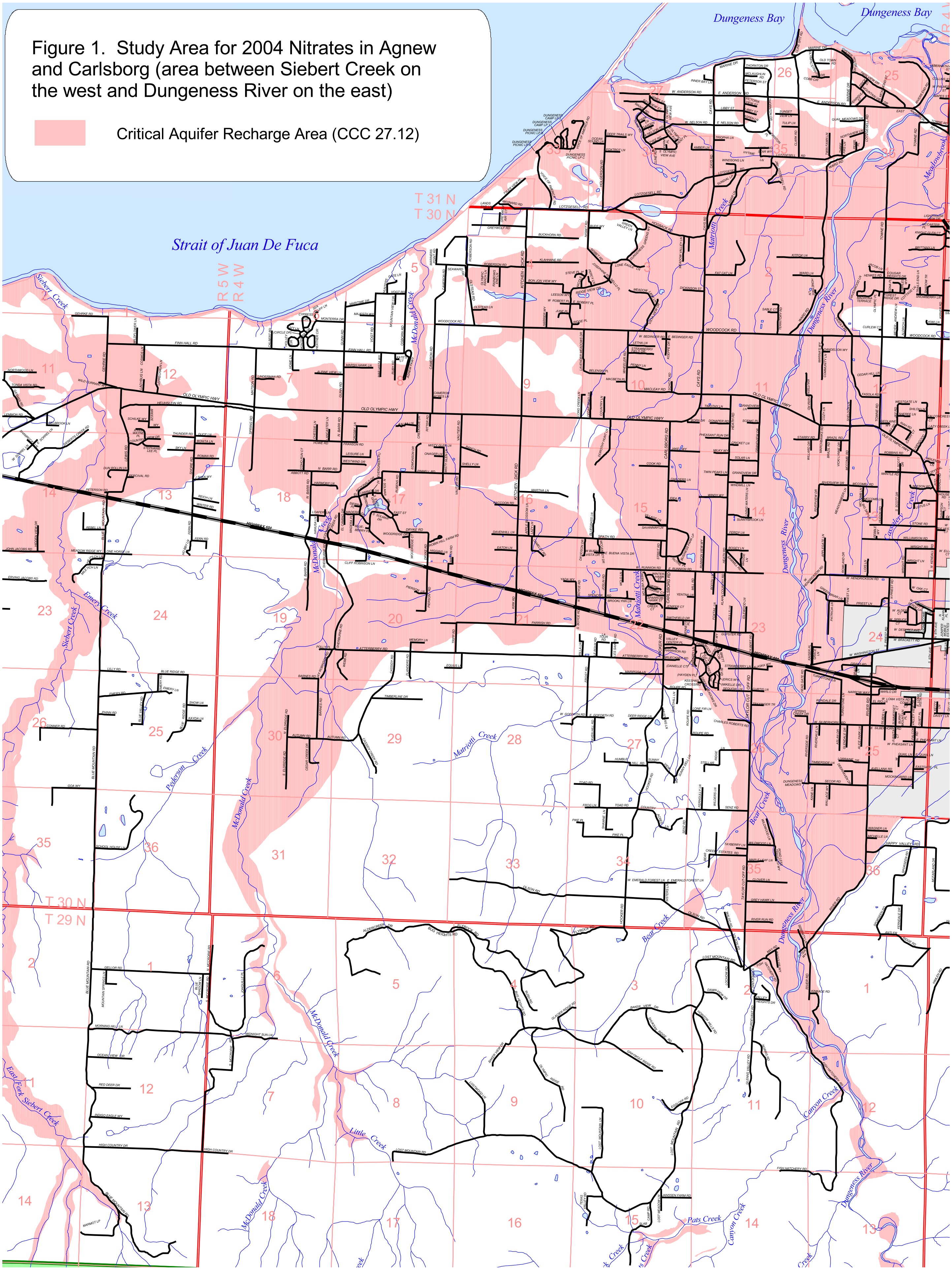


Figure 1. Study Area for 2004 Nitrates in Agnew and Carlsborg (area between Siebert Creek on the west and Dungeness River on the east)

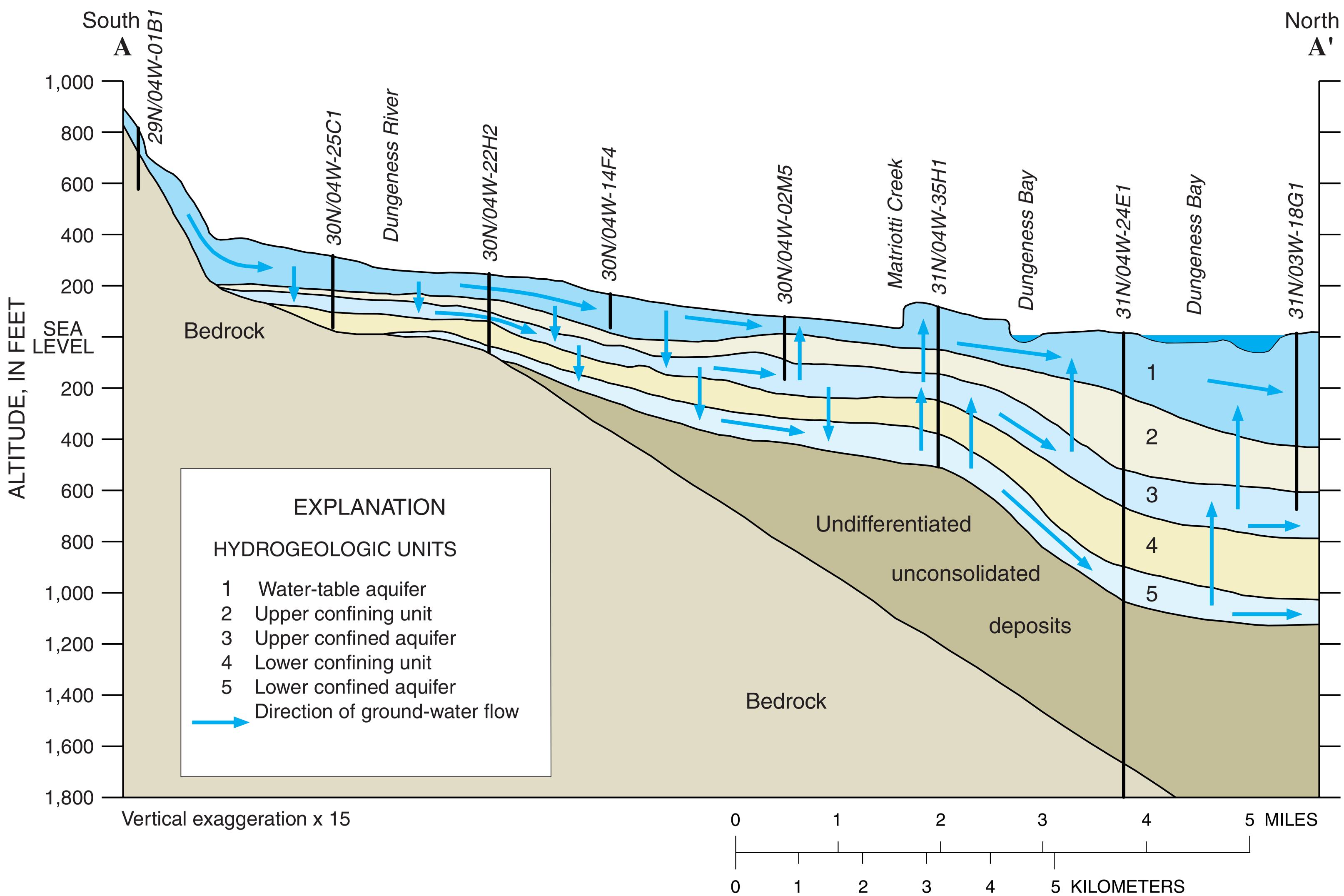
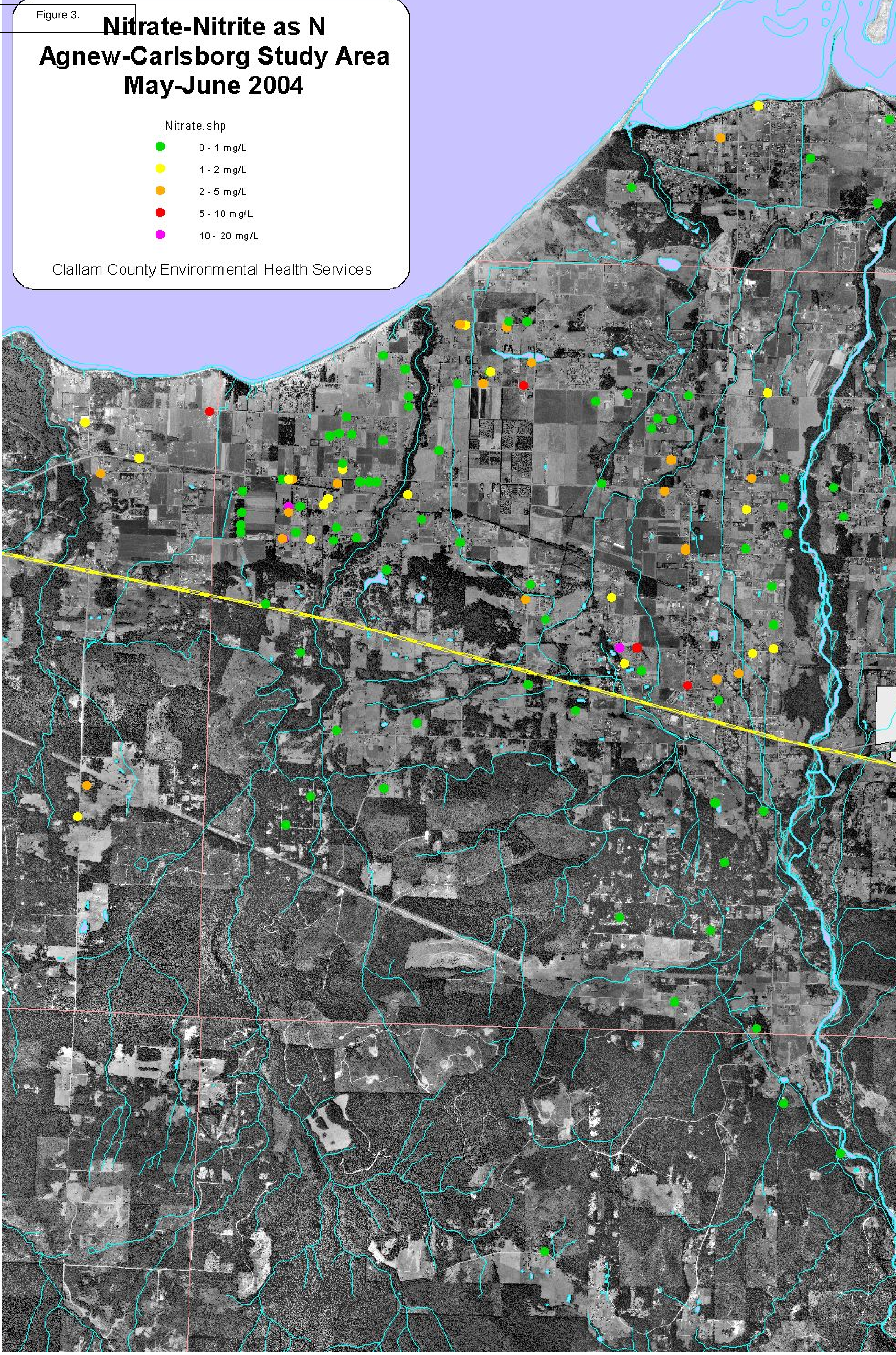


Figure 2. Hydrogeologic section showing the principal aquifer and confining units and directions of ground-water flow on the Sequim-Dungeness peninsula, Clallam County, Washington.

(from Simonds and Sinclair 2002; modified from Drost, 1983)

Figure 3.


Nitrate-Nitrite as N
Agnew-Carlsborg Study Area
May-June 2004
Nitrate.shp
0 - 1 mg/L
1 - 2 mg/L
2 - 5 mg/L
5 - 10 mg/L
10 - 20 mg/L
Clallam County Environmental Health Services

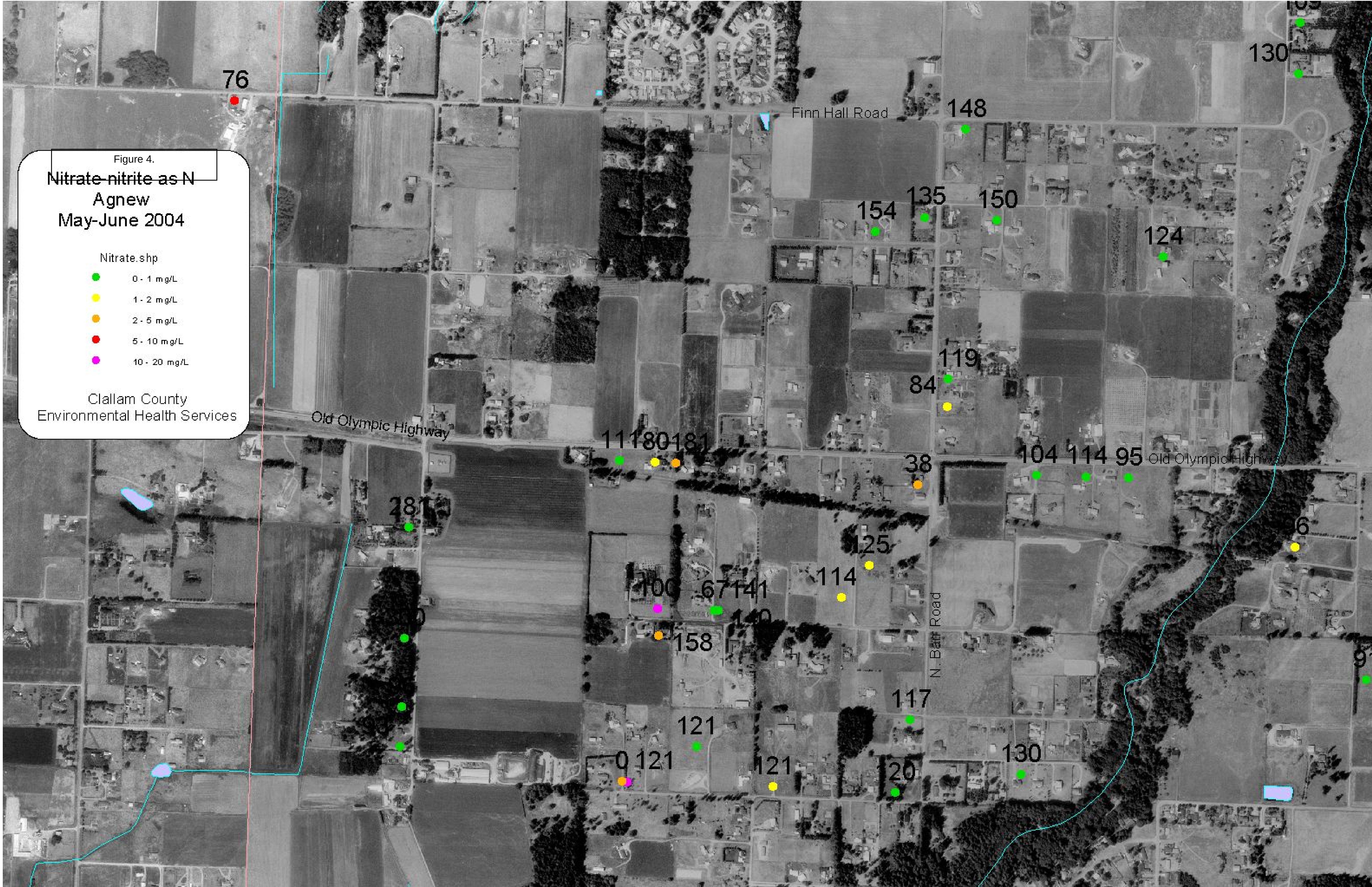


Figure 4.
Nitrate-nitrite as N
Agnew
May-June 2004
Nitrate.shp
0 - 1 mg/L
1 - 2 mg/L
2 - 5 mg/L
5 - 10 mg/L
10 - 20 mg/L
Clallam County
Environmental Health Services
Finn Hall Road
Old Olympic Highway
Old Olympic Highway
N. Barr Road
76
148
130
135
150
154
124
119
84
111
80
181
38
104
114
95
281
125
114
100
67
141
140
158
117
121
0
121
121
120
130
91

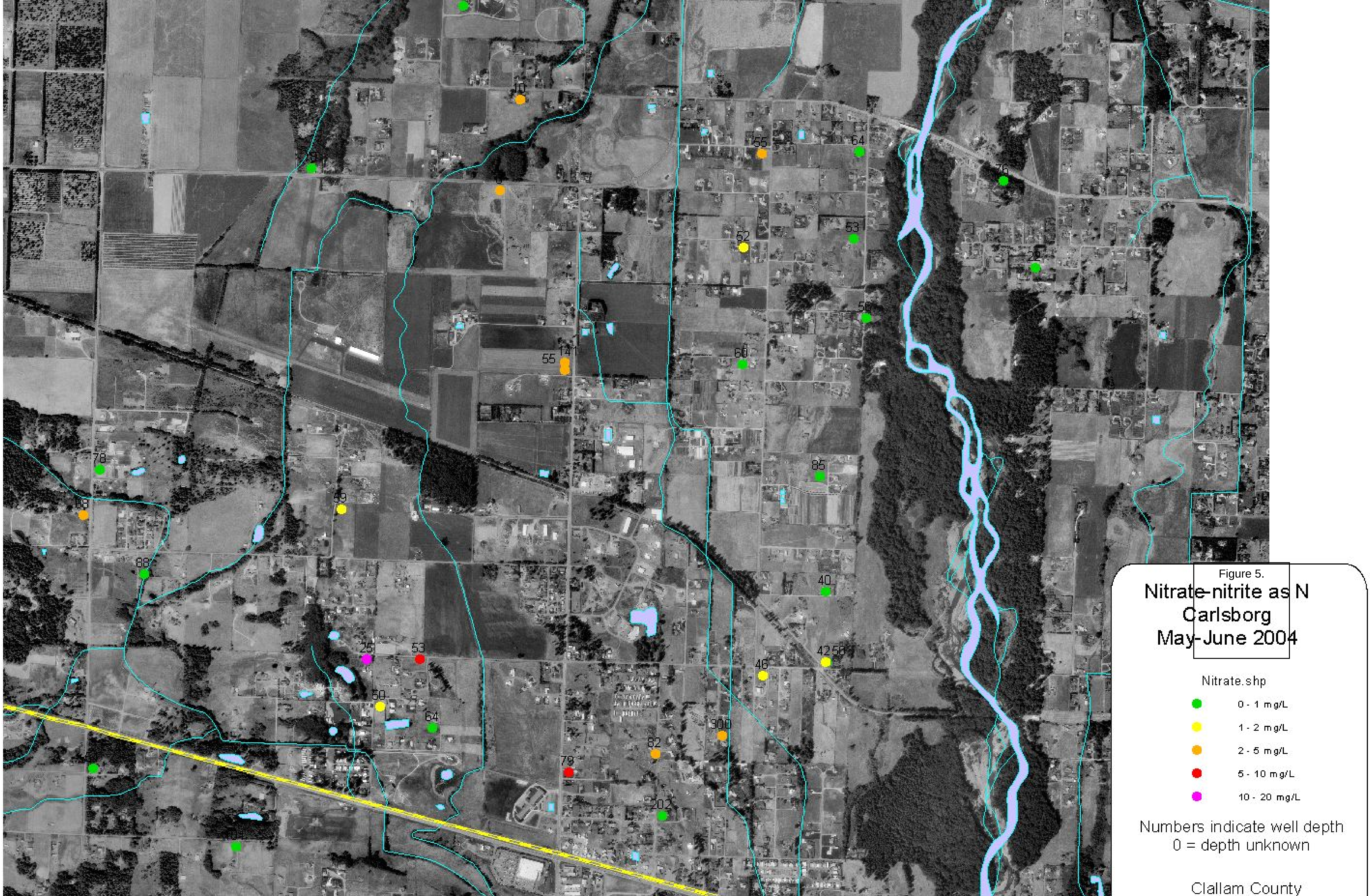


Figure 5.
Nitrate-nitrite as N
Carlsborg
May-June 2004

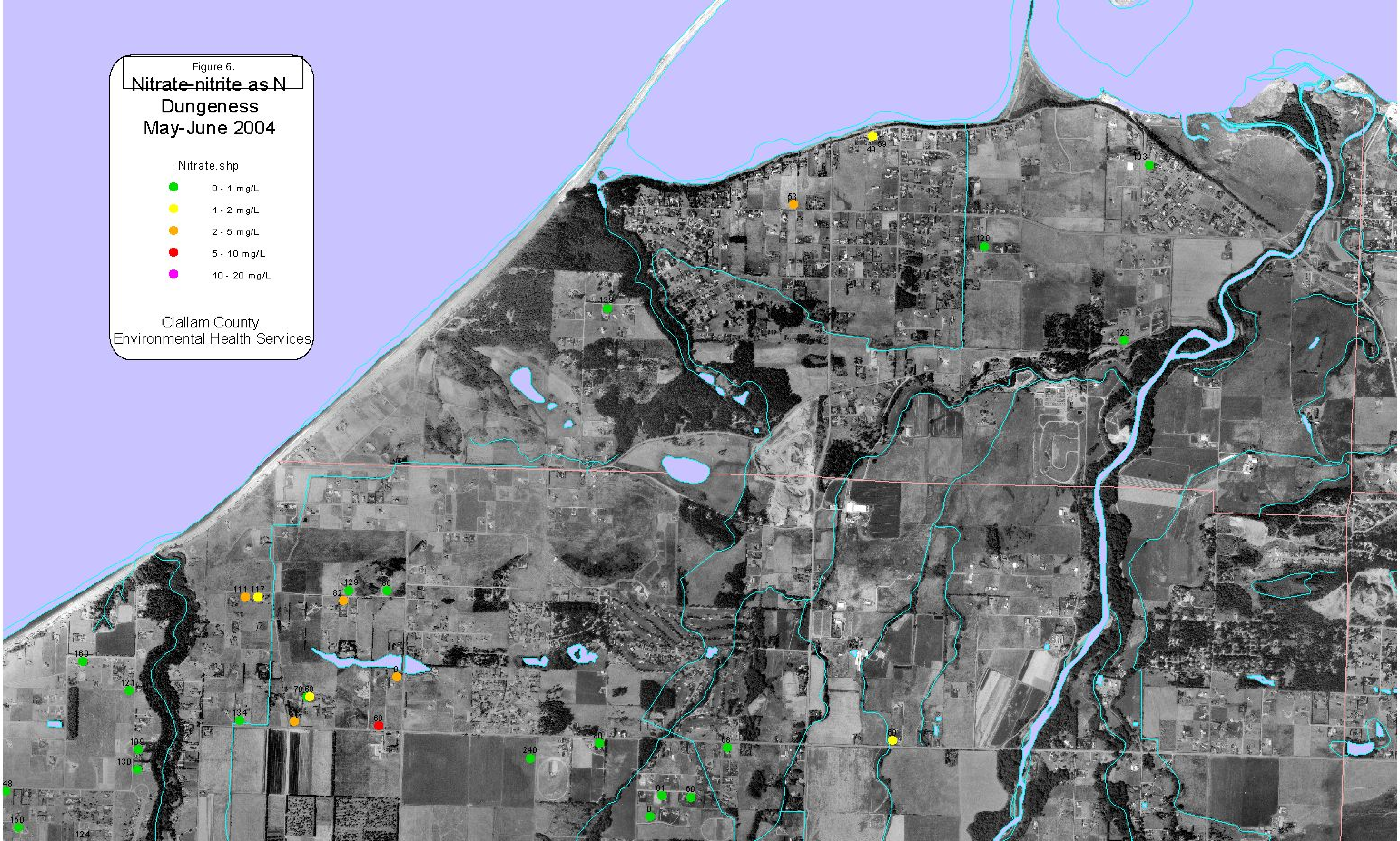


Figure 6.
Nitrate-nitrite as N
Dungeness
May-June 2004
Nitrate.shp
0 - 1 mg/L
1 - 2 mg/L
2 - 5 mg/L
5 - 10 mg/L
10 - 20 mg/L
Clallam County
Environmental Health Services

Appendix A: Summary of information on study wells

Bottle #	Date	Time	Nitrate + Nitrite as N (mg/L)	Sampled by	Well ID, if available	Well depth	Year drilled	Source of well construction info	Gone dry?	Yard fertilizers or chemicals used? (Never/Sometimes/ Occasionally)
1-37	5/20/04	3:00pm	1.40	owner	31N/04W-26M02	59		USGS	N	N
1-5	5/20/04	3:00pm	1.39	owner	31N/04W-26M01	49		USGS	N	N
1-3	5/21/04	10:10am	0.33	owner		45	1990	Taken off well log	N	S - both
1-27	5/21/04	10:59am	0.07	owner		56	1991	Taken off well log	N	N
1-29	5/21/04	11:32am	1.60	owner		96	1991	Taken off well log	N	S - both
1-23	5/21/04	8:30am	0.02	owner	30N/04W-11R06	22	1978?	USGS	N	S- fertilizers
1-20	5/21/04	9:08am	1.12	owner		60	1993	Taken off well log	N	N
1-2	5/21/04	9:15am	0.04	owner		148	1978	Taken off well log	N	S herbicides
1-14	5/27/04	2:30	<0.01	owner	ABB006	137	1996	Taken off well log	N	S - both
1-10	5/27/04	3:53	<0.01	owner		109	1981	Taken off well log	N	S- both
2-4	5/27/04	13:20	<0.01	owner		130	1993	Measured	N	N - both
2-46	5/27/04	15:19	2.44	owner		unknown	1977		N	N
2-47	5/27/04	1:36pm	2.73	owner		65	1961	Informed by previous owner	N	S- both
2-14	5/27/04	1:45pm	0.39	owner		120	1989	Informed by previous owner	N	N-fert S - herb
2-40	5/27/04	1:55pm	1.75	owner		63	1983	Taken off well log	N	S - both
2-22	5/27/04	11:50am	1.43	owner	AB0741	42	1998	Informed by previous owner	N	S - fert N - herb
1-13	5/27/04	12:30pm	<0.01	owner		119		Taken off well log	N	N - both
2-44	5/27/04	2:04pm	0.15	owner		53	1997	Taken off well log	N	S - both
1-33	5/27/04	2:15pm	0.03	owner		75-80	1977	Informed by previous owner	Unknown	S - both
2-45	5/27/04	2:15pm	<0.01	owner	AFE548	160	2002	Taken off well log	N	N
2-38	5/27/04	2:20pm	<0.01	owner		68	1997	Taken off well log	N	S - both
2-19	5/27/04	2:27pm	0.16	owner		64	1996	Taken off well log	N	S - both
A-5	5/27/04	2:35pm	0.06	owner	30N/04W-04N04	70	1980	USGS	N	N - both
2-27	5/27/04	2:35pm	0.06	owner		86	1998	Taken off well log	N	N
2-16	5/27/04	2:40pm	<0.01	owner	AFT550	240	2001	Taken off well log	N	N - both
2-7	5/27/04	2:41pm	6.00	owner		76	1946	Informed by previous owner	Y 2-3 years ago	S -both
2-10	5/27/04	2:45pm	3.18	owner		158	2003	Taken off well log	N	O - fert S - herb
1-12	5/27/04	2:46pm	4.53	owner	30N/04W-15G03	55		USGS	N	N - both
2-29	5/27/04	2:55pm	0.02	owner		61	1999	Taken off well log	N	S - both
311	5/27/04	2:55pm	18.9	owner		100		?		
2-13	5/27/04	3:00pm	0.13	owner		111	1978	Taken off well log	N	N - both
2-39	5/27/04	3:00pm	0.62	owner	30N/04W-21G03	54	1978	Taken off well log	N	S-fert N - herb
2-41	5/27/04	3:06pm	0.01	owner		176	70's-80's	Measured	N	N -both
2-34	5/27/04	3:17pm	<0.01	owner		50	1975	Taken off well log	N	N - both
2-42	5/27/04	3:44pm	12.5	owner		121	1992	Taken off well log	N	N - both
2-37	5/27/04	3:45pm	3.15	owner		68	1963	Taken off well log	N	S - both
2-48	5/27/04	3:50pm	1.09	owner		117	1976	Taken off well log	N	O - fert S - herb
2-9	5/27/04	3:52pm	1.49	owner		84		Measured	N	S - both
2-8	5/27/04	4:00pm	<0.01	owner		96	1991	Taken off well log	N	S - both
2-15	5/27/04	4:23pm	<0.01	owner		183	1984	Taken off well log	N	N - both
1-7	5/27/04	4:25pm	<0.01	owner	ABP666	150	1999	Taken off well log	N	N - fert S -herb
1-35	5/27/04	4:40pm	0.23	owner		93-97	1988	Taken off well log	N	N - both
2-2	5/27/04	4:50pm	<0.01	owner	30N/04W-05H71	134	1990	Taken off well log	N	S - both
A-1	5/27/04	5:00pm	0.70	owner	30N/04W-17B01	91	1974	Taken off well log	N	S - fert N - herb

Appendix A: Summary of information on study wells

Bottle #	Date	Time	Nitrate + Nitrite as N (mg/L)	Sampled by	Well ID, if available	Well depth	Year drilled	Source of well construction info	Gone dry?	Yard fertilizers or chemicals used? (Never/Sometimes/ Occasionally)
2-12	5/27/04	5:30pm	1.11	owner		80	1920	Informed by previous owner	Y unknown timing	N - both
320	5/28/04	1:25pm	<0.01	owner		129	1996	Taken off well log	N	
309	5/28/04	10:15am	<0.01	owner	ACR142	33	1999	Informed by previous owner	N	S - both
1-17	5/28/04	10:17am	2.65	owner	30N/04W-05J02	111	1976	Taken off well log	N	N -fert S - herb
2-23	5/28/04	12:20pm	0.27	owner	31N/04W-25N05	103		USGS		N - fert S - herb
2-31	5/28/04		<0.01	owner		unknown				
2-25	5/29/04	2:41pm	0.78	owner		60	1994	Taken off well log	N	S - both
30-4-22D72	6/1/04	12:15	0.05	EHS staff	30N/04W-22D72	about 35		Owner	N	N
A-2	6/01/04	10:20am	<0.01	owner	30N/04W-07N01	281		USGS		
A-8	6/01/04	12:15pm	14.9	owner	30N/04W-22D71	25		Measured	N	N - both
2-43	6/01/04	6:30am	0.10	owner		120	1974	Taken off well log	N	N - fert S - herb
2-5	6/01/04	6:58am	0.12	owner		140	1993	Taken off well log	N	N - both
1-24	6/01/04	7:30am	4.98	owner	30N/04W-04N01	51		USGS		
1-8	6/01/04	8:10am	<0.01	owner		154	1988	Taken off well log	N	S -both
307	6/02/04	1:00pm	0.30	owner		114	1996	?	N	S - both
423	6/02/04	1:18pm	1.15	owner		121	1996	Taken off well log	N	S - both
318	6/02/04	10:35am	<0.01	owner		88	1984	Taken off well log	N	N - fert S - herb
319	6/02/04	12:10pm	1.39	owner		52	1989	Taken off well log	N	S - both
2-35	6/02/04	2:15pm	1.18	owner		114		Taken off well log	N	S - both
2-26	6/02/04	8:35am	0.68	owner		178		Measured	N	S - both
1-30	6/02/04	8:36am	<0.01	owner	AFT593	148	2001	Taken off well log	N	S - both
310	6/02/04	8:37am	1.51	owner		65	1960	?	N	N - both
2-21	6/02/04	8:40am	0.41	owner		635	1994	Taken off well log	N	N- fert S- herb
2-20	6/02/04	8:44am	0.42	owner		244	1994	Taken off well log	N	N - fert S - herb
1-28	6/02/04	9:55am	4.76	owner	AFT526	141	2001	Taken off well log	N	N - both
30-4-8J1	6/3/04	14:13	0.53	EHS staff	30N/04W-08J01	56	1960	USGS	N	
305	6/03/04	10:00am	<0.01	owner		130	1970?	Informed by previous owner	N	N - both
1-11	6/03/04	10:16am	1.67	owner	AFA367	121	1999	Taken off well log	N	N - fert S - herb
501	6/03/04	11:41am	0.02	owner		85		Informed by previous owner	N	N - both
1-15	6/03/04	12:10pm	<0.01	owner		135	1983	Taken off well log	N	S - both
2-32	6/03/04	12:10pm	0.48	owner		101	1976	Taken off well log	N	N - both
2-24	6/03/04	12:30pm	1.00	owner		63.5	1986	Taken off well log	N	S - both
408	6/03/04	12:30pm	<0.01	owner	30/N04W-18D74	93	1995	Taken off well log	N	S - both
315	6/03/04	12:55pm	0.38	owner		40		Measured	N	N - fert S - herb
502	6/03/04	5:00pm	<0.01	owner		300	2002	Informed by previous owner	N	S - both
2-18	6/03/04	6:50am	0.49	owner		50	1973	Informed by previous owner	N	S - both
321	6/03/04	7:47am	0.25	owner		60	1995	Informed by previous owner	N	S - both
2-6	6/03/04	8:00am	4.10	owner		90	1976	Taken off well log	N	N - both
405	6/03/04	8:25am	0.32	owner		39	1984	?	N	N - both
308	6/03/04	8:30am	0.27	owner		98	1993	Taken off well log	N	N - both
417	6/03/04	9:00am	0.10	owner		121	1973	Informed by previous owner		N - both
409	6/03/04	9:33am	<0.01	owner		124	1993	Taken off well log	N	N - both0
426	6/03/04	9:50am	0.32	owner	30N/04W-23E03	202		USGS		

Appendix A: Summary of information on study wells

Bottle #	Date	Time	Nitrate + Nitrite as N (mg/L)	Sampled by	Well ID, if available	Well depth	Year drilled	Source of well construction info	Gone dry?	Yard fertilizers or chemicals used? (Never/Sometimes/ Occasionally)
407	6/04/04	10:25am	2.31	owner		10		Measured	N	N - both
413	6/04/04	10:30am	0.04	owner		275	1993	Informed by previous owner	N	S - fert N - herb
1-1	6/04/04	10:40am	6.25	owner		53	2001	Taken off well log	N	N - both
410	6/04/04	10:42am	1.40	owner		86		Measured	N	
422	6/04/04	10:45am	1.41	owner		125	1995	Taken off well log	N	S - both
401	6/04/04	10:50am	2.13	owner	31N/04W-27R01	53		Taken off well log	N	O - fert S - herb
420	6/04/04	10:54am	0.66	owner		74	1992	Taken off well log	N	N - both
A-7	6/04/04	10:55am	0.09	owner	30N/04W-11J01	76	1976	USGS	N	S - fert N - herb
414	6/04/04	10:57am	0.02	owner	AFT518	119	2001	Taken off well log	N	N - fert S - herb
421	6/04/04	11:00am	1.16	owner		46	1991	?	N	S - both
416	6/04/04	11:00am	0.20	owner		104		?		
504	6/04/04	11:03am	<0.01	owner		139	1991	Taken off well log	N	
419	6/04/04	11:09am	0.02	owner		67	1988-89	Informed by previous owner	N	N - both
425	6/04/04	11:15am	2.08	owner		55	1995	?	N	S - fert N - herb
503	6/04/04	11:15am	0.40	owner		70	1995	Informed by previous owner	N	N - both
A-12	6/04/04	11:20am	4.03	owner		unknown	1983		N	N - both
A-4	6/04/04	11:30am	9.48	owner	30N/04W-22H72	79		Taken off well log	N	N - both
2-28	6/04/04	8:23am	0.78	owner		113	1993	Taken off well log	N	N - both
A-11	6/04/04	8:57am	4.13	owner	30N/04W-04P91	unknown	1972		N	S - both
A-10	6/04/04	9:19am	7.11	owner	30N/04W-04P92	60	1972	Measured	N	N - both
A-3	6/04/04		0.37	owner		117	1981	Taken off well log	N	
418	6/10/04	1:47pm	1.36	owner		50	1992	?	N	N - both
317	6/10/04	10:12am	1.19	owner		59	1991	Taken off well log	N	S - fert N - herb
304	6/10/04	12:20pm	<0.01	owner		111	1978	Taken off well log	N	O - fert N - herb
303	6/10/04	12:54pm	0.68	owner		141	1994	Taken off well log	N	N - both
2-11	6/10/04	7:55am	3.37	owner		35-40		?	N	N - both
1-26	6/11/04	10:00am	2.05	owner		82	1992	?	N	S - both
424	6/11/04	10:30am	2.93	owner		181	1995	Taken off well log	N	N - both
411	6/11/04	11:14am	<0.01	owner		42	1988-89	?	N	S - both
313	6/11/04	11:15am	<0.01	owner		18		?	N	N - both
2-3	6/11/04	11:17am	0.25	owner	AGN279	121	2002	Taken off well log	N	N - both
406	6/11/04	11:18am	3.58	owner		300		Informed by previous owner	N	S - fert O - herb
1-18	6/11/04	11:30am	0.05	owner		123	1984	Taken off well log	N	S - both
322	6/11/04	7:10am	4.20	owner		82		?	Y 2001	
505	6/11/04	7:58am	0.07	owner		195	1991	Taken off well log	N	N - both
2-17	6/11/04	8:15am	<0.01	owner		80		?	N	S - both
1-36	6/11/04	9:45am	0.01	owner		110-125	1975-77	Informed by previous owner	N	S - both
2-36	6/11/04	9:56am	0.03	owner		24	1989	Informed by previous owner	N	S - both

APPENDIX B. Nitrate data quality assessment

I. PRECISION

Measurement Quality Objective = 10%

A. Total Precision (replicate field samples)

1. Relative Percent Difference (RPD)

Dupe pairs	non-neg Diff	x200	C1 + C2	%RPD
14.6	0.1	20	29.30	**0.68**
14.7				
3.95	0.04	8	7.94	**1.01**
3.99				
0.05	0.01	2	0.11	**Don't use because precision can't be accurately estimated when results are very near detection limit.**
0.06				
0.02	0	0	0.04	**Don't use because precision can't be accurately estimated when results are very near detection limit.**
0.02				

2. Relative Standard Deviation (RSD)
Pooling estimates of standard deviation for pairs (use when dupe pairs are of the same order of magnitude)

Dupe pair 1	non-neg Diff	D squared	Sum of D squareds	2m	Divided	**Sp**	**RSD**
14.6	0.10	0.01					0.367588041
14.7			0.0116	4	0.0029	**0.05385165**	
3.95	0.04	0.0016					1.354758442
3.99							

Dupe pair 2	non-neg Diff	D squared	Sum of D squareds	2m	Divided	**Sp**	**RSD**
0.05	0.01	0.0001					9.090909091
0.06			0.0001	4	0.000025	**0.005**	
0.02	0.00	0	**Don't use because precision can't be accurately estimated when results are very near detection limit.**				
0.02							

APPENDIX B. Nitrate data quality assessment

B. Analytical Precision (replicate lab analysis of samples)

	Duplicates		**1. Relative Percent Difference**	**2a. Standard Deviation**	
	Sample result	Dupe result	**%RPD**	**s**	**RSD**
Batch 1	0.39	0.39	0	0	0
Batch 2	2.1	2.2	4.6	0.070710678	3.28886875
Batch 3	0.3	0.29	3.4	0.007071068	2.39697214
Batch 4	0.43	0.43	0	0	0

2b. Pooling estimates of standard deviation for pairs (use when dupe pairs are of the same order of magnitude)

Dupe pairs	non-neg Diff	D squared					**RSD**
0.39	0.00	0	Sum of D squareds	2m	Divided	**Sp**	1.046790488
0.39			0.0001	6	1.6667E-05	**0.00408248**	
0.3	0.01	0.0001					1.38389251
0.29							
0.43	0	0					0.949414629
0.43							

II. ANALYTICAL BIAS

Measurement Quality Objective = within 10% of true value

		Blank	**Lab Check Standard**			
	n	NO3+NO2	Value	Lab Result	**% Recovery**	**Bias**
Batch 1	8	<0.01	3.07	3.06	99.7	-0.3
Batch 2	47	<0.01	3.07	3.16	103	3
Batch 3	73	<0.01	17.4	17.5	101	1
Batch 4	17	<0.01	17.4	17.6	101	1

APPENDIX B. Nitrate data quality assessment

III. ACCURACY

Measurement Quality Objective = 30% deviation from true value

	Precision RSD	Bias	Accuracy	= (Precision x 2) + Bias
Batch 1	0	-0.3	-0.3	
Batch 2	3.28886875	3	9.5777375	
Batch 3	2.39697214	1	5.7939443	
Batch 4	0	1	1	

IV. COMPLETENESS

Measurement Quality Objective = 90%

145 samples analyzed
145 valid analyses
= 100%

V. DIFFERENCES IN STAFF VS. PUBLIC SAMPLING

Paired comparison t-test for difference between staff and public sampling (includes all pairs less than 10 days apart)

Dupe pairs	Diff (non-neg)	Coded diff	D squared
2.07	0.06	0.60	0.36
2.13			
10.1	0.62	6.20	38.44
9.48			
0.71	0.01	0.10	0.01
0.70			
0.38	0.01	0.10	0.01
0.37			
0	0.06	0.60	0.36
0.06			
0.31	0.01	0.10	0.01
0.32			
14.7	0.20	2.00	4.00
14.9			
0.02	0.02	0.20	0.04
0			
0.1	0.01	0.10	0.01
0.09			
0.03	0.03	0.30	0.09
0			
3.97	0.06	0.60	0.36
4.03			

n	**Sum of D**	**Sum of D squared**	**s**	**t**	**degrees of freedom**
11	10.90	43.69	1.81	1.9	10

t (0.05)
2.228

The observed value (1.9) is less than the tabulated value (2.28), therefore there is no significant difference.